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# Investigations into the mechanisms for the formation of primary olefins from methanol over ZSM-5 zeolite catalysts

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## 1. Scope

There exist three fundamental challenges on the conversion of methanol to hydrocarbons (MTH) over zeolite catalysts: (i) the identification of the primary reactant as methanol and its anhydrous equilibrium product, dimethyl ether (DME) initially compete for active sites, (ii) the first olefin formed and (iii) the dominating mechanism leading to it. Direct mechanisms involving surface carbene, tri-methyloxonium ion, methyl ethyl ether, methane-formaldehyde and CO and indirect mechanisms involving impurities (acetone or ethanol) have been suggested. These mechanisms lead to the pre-formation of a hydrocarbon pool which is responsible for steady state MTH conversion. The primary product (ethene and/or propene) has been shown to vary with Si/Al ratios and outlet DME/methanol ratios.<sup>1</sup> In this contribution, the influence of mass transfer on product distribution is elucidated and a Langmuir-Hinshelwood-Hougen-Watson kinetic model using a lumped methodology is used to study the conversion of methanol and DME to hydrocarbons when tuned towards gasoline (1 bar, 370°C) and olefin formation (1 bar, 450°C) over ZSM-5 catalysts.

## 2. Experimental

Anhydrous DME (99.99 vol%), methanol (99.93 wt%), NH<sub>4</sub>-ZSM-5 (Si/Al=36) powder with particle diameter of 10µm and NH<sub>4</sub>-ZSM-5 (Si/Al=34) after being pressed, crushed and sieved to give particles sizes of 250 – 500 µm were used. The protonic forms were obtained by thermal treatment under 30 vol% O<sub>2</sub>/N<sub>2</sub>. The product gases were insulated and sampled through an online gas chromatography–flame ionization detector equipped with an Equity™ –1 fused silica capillary column. Internal and external heat and mass transfer effects were checked using experimental criteria such as Wheeler-Weisz modulus, Carberry number and the internal and external Prater numbers. A lumped kinetic model involving 45 species and intermediates and 252 parameters was built using MATLAB to study the dominating mechanism that controls product distribution. Sensitivity analysis technique was used to reduce the number of parameters. Parameter optimization was carried out using the Levenberg-Marquardt routine and confidence intervals were obtained using Monte-Carlo methods.

## 3. Results and discussion

MTH conversion was first studied using 25 wt% inlet methanol feed at 370°C with ZSM-5 (Si/Al=34). Methanol transformation shows autocatalytic behaviour as shown by the S-shaped curve (Figure 1). The S-shaped curve shows the initial characteristic induction phase at low conversions, the intermediate autocatalytic regime and slow termination phase at high conversions. The presence of an induction phase supports the initial transformation of methanol through a high activation energy barrier particularly *via* the direct mechanisms. During the induction phase (up to 5% conversion), the formation of aromatics and paraffins were minimal indicating that the formation of primary olefins and the methylation of olefins controlled the product distribution. Ethene and propene were formed initially at approximately equal yields (Figure 2). The analysis of the experimental criteria showed that the reaction kinetics were affected by external heat and mass transfer as well as internal mass transfer limitations.

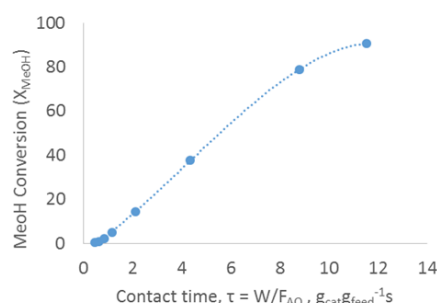


Figure 1: Evolution of methanol at full conversions

Further studies compared MTH conversion using inlet feeds of 1 wt% DME to 1 wt% methanol. At contact times less than  $2 \text{ g}_{\text{cat}}\text{g}_{\text{feed}}^{-1}\text{s}$ , conversions of less than 15% were obtained (Figure 3). At low conversions with 1 wt% methanol feed, internal and external heat and mass transfer limitations were negligible. Twice the contact time for similar methanol conversions at  $370^\circ\text{C}$  was required than at  $450^\circ\text{C}$ . Propene was the major olefin formed over ZSM-5 (Si/Al=36) at both temperatures, although methane was the first product observed (Figure 4,5). This observation supports the proposal that ethene, which has been linked to the dominance of the aromatic cycle at low conversions<sup>2</sup> is formed under mass transfer limitations. With an inlet feed of 1 wt% DME, propene, butene and pentene are still the major olefins formed. However, analysis of experimental criteria shows that internal and external mass transfer affected the reaction kinetics due to low DME diffusivities and mass transfer coefficients respectively. Nonetheless, the mass transfer limitations due to DME does not suggest that methanol which is formed via initial equilibration is also under transport limitations. It is evident that ethene is formed primarily

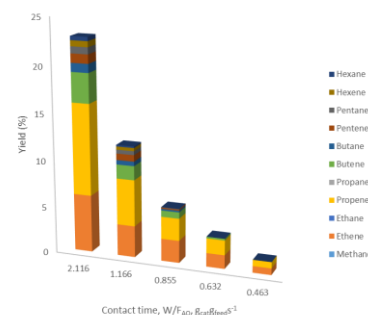


Figure 2: Conversion of 25wt% inlet methanol at  $370^\circ\text{C}$

from methanol which propagates the aromatic cycle while DME propagates the olefin cycle. The contribution of paraffin cracking towards methane formation from methanol is minimal at  $370^\circ\text{C}$  and at low conversions. Methane can only form simultaneously alongside olefin formation.

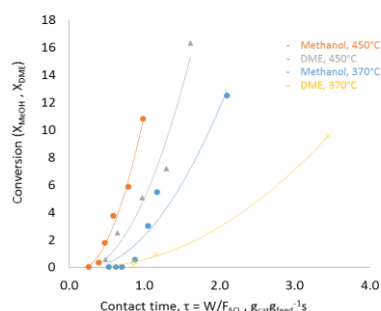


Figure 3: Comparison of 1wt% inlet methanol feed to 1wt% DME feed

The controlling mechanism at low conversions with a feed of 1 wt% methanol and 1 wt% DME using the kinetic model was investigated. The decomposition of methanol and DME and subsequent carbonylation is investigated as it leads to simultaneous formation of methane and primary olefins with a low energy barrier pathway.<sup>3</sup>

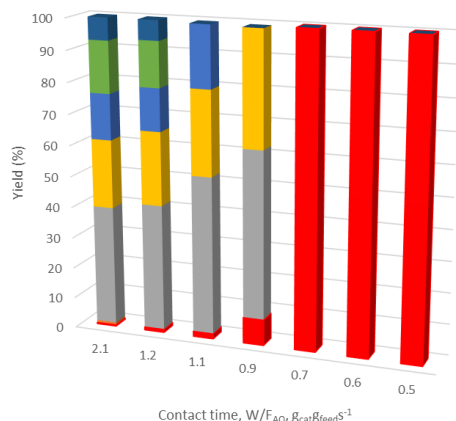


Figure 4: Conversion of 1wt% inlet methanol at  $370^\circ\text{C}$

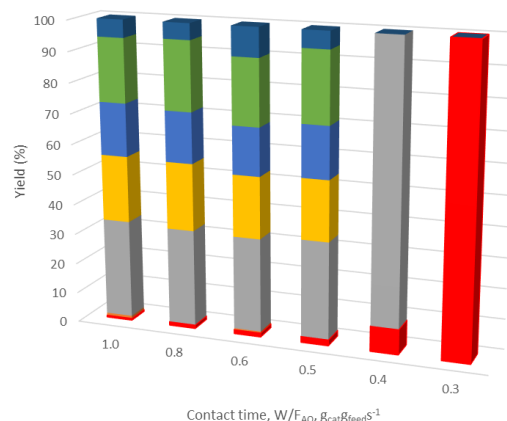


Figure 5: Conversion of 1wt% inlet methanol at  $450^\circ\text{C}$

## 4. Conclusions

Here, it is shown that under transport limitations, ethene is formed as a primary product from methanol while DME propagates the olefin cycle. A comprehensive study that considers the influence of initial rate on pressure and temperature and discriminates between adsorption, desorption, and activity control in combination with Maxwell-Stefan equations for each specie during the transformation of methanol and DME to hydrocarbons is underway and likely to provide clearer insights into transport effects on intrinsic kinetics.

## 5. References

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